

Note: The stream numbers on the figure correspond to the discussion in the text for this process. Letters correspond to potential sources of benzene emissions.

Figure 6-9. Process Flow Diagram for Manufacture of Synthetic Graphite

Source: Reference 174.

stock." The green stock is placed in cooling ponds, where it is further cooled and awaits shipping to the baking process. 175

In general, for producing graphite with high-performance applications, the baking process consists of three stages: initial baking, pitch impregnation, and rebaking. In producing graphite for some lower-performance applications, the pitch impregnation step is excluded. This baking process chemically changes the binder pitch within the green stock by forming a permanent carbon bond between the coke particles. By using a slow heating rate, the baking process removes most of the shrinkage in the product associated with pyrolysis of the pitch binder. This procedure avoids cracking during subsequent graphitization where very fast firing rates are used. The impregnation step deposits additional coke in the open pores of the baked stock, thereby improving the properties of the subsequent graphite product. The product (later referred to as "rebaked stock") is a solid, rigid body that is much harder and stronger than the green stock.^{174,175}

Initial baking is achieved by placing the green stock into a furnace cell (if a recirculating furnace is used) or a can (if a sagger or pit furnace is used) and surrounding the stock with a suitable pack media to support the stock. During the baking process, the furnace temperature is increased incrementally (e.g., starting at 350 to 400°F [175 to 200°C] and ending at 400 to 570°F (200 to 300°C]). The furnace temperature varies according to the stock. During the initial baking process, fumes (Vent C in Figure 6-9) are often vented to an afterburner prior to discharge to the atmosphere.¹⁷⁵

Baked stock is pre-heated in a pre-heater to a desired temperature prior to impregnation with pitch. Fumes from the pre-heater (Vent D in Figure 6-9) are often vented to an afterburner before release to the atmosphere. The pre-heated, baked stock is loaded into autoclaves where a vacuum is pulled. Heated petroleum pitch (or coal tar) is pumped from storage to the autoclave. Vapors from the storage tank for the heated pitch (Vent D in Figure 6-9) are often vented to an afterburner prior to their release to the atmosphere. The baked stock is impregnated with pitch under increased temperature and pressure. The pitch

impregnated stock is then stored prior to the rebaking process. Many high-performance applications of graphite (e.g., nuclear and aerospace applications) require that the baked stock be multiply pitch-treated to achieve the greatest possible assurance of high performance.^{174,175}

Rebaking is similar to initial baking. The same types of furnaces are used for both baking and rebaking. The pitch impregnated stock is heated to higher temperatures than the green stock (e.g., from $210^{\circ}F$ [$100^{\circ}C$] to 900 to $1,800^{\circ}F$ [500 to $1,000^{\circ}C$]). During the rebake process, fumes (Vent E in Figure 6-9) are often vented to an afterburner. Off-gases from the afterburner are vented to the atmosphere. 174,175

The last step in the manufacturing process is graphitization. In this step, electricity is used to create temperatures, by resistance, high enough to cause physical and chemical changes in the rebaked stock (the carbon atoms in the petroleum coke and pitch orient into the graphite lattice configuration). As a result of this step, the hard-baked stock becomes softer and machinable, the stock becomes an electrical conductor, and impurities vaporize. 174,175

In the graphitization step, rebaked stock is placed in a furnace, either perpendicular or parallel to the direction of the current flow, depending on the type of furnace used. Electricity is used to create temperatures in the stock exceeding 4,350°F (2,400°C), and preferably 5,070 to 5,450°F (2,800 to 3,000°C). After graphitization, the stock (i.e., synthetic graphite) is stored for on-site use or shipment. Fumes from the furnace are vented to the atmosphere (Vent F in Figure 6-9). 174,175

6.8.2 <u>Benzene Emissions from Synthetic Graphite Production</u>¹⁷⁵

There is limited information currently available about benzene emissions from synthetic graphite production plants. Emission factors for the mixing and cooling cylinders (Vents A and B in Figure 6-9) are provided in Table 6-27. Additionally, one emission test report indicated that benzene is emitted from the initial baking, rebaking, and

TABLE 6-27. EMISSION FACTORS FOR SYNTHETIC GRAPHITE PRODUCTION

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/lb (g/kg) ^a	Emission Factor Rating
3-XX-XXX-XX	Synthetic Graphite	Mixing Cylinder (Vent A)	Uncontrolled	2.82x10 ⁻⁴ (1.41x10 ⁻⁴)	D
3-XX-XXX-XX	Synthetic Graphite	Cooling Cylinder (Vent B)	Uncontrolled	3.70x10 ⁻⁴ (1.8x10 ⁻⁴)	D

Source: Reference 175.

^a Emission factor is lb (g) of benzene emitted per lb (kg) of synthetic graphite produced.

pitch-impregnation processes (Vents C through E in Figure 6-9); however, emission factors could not be developed.¹⁷⁵

6.8.3 <u>Control Technologies for Synthetic Graphite Production</u>¹⁷⁵

As discussed in Section 6.9.1, afterburners may be used to control emissions of unburned hydrocarbons from the initial baking and rebaking furnace (Vents C and E in Figure 6-9), as well as the preheater and heated storage tank used for the pitch impregnation process (Vent D in Figure 6-9). Data regarding the use of afterburners in this application were not available; however, it is likely that the afterburners would reduce benzene emissions. Additionally, an ESP may be used to control particulate emissions from the cooling cylinder; however, it is unlikely that an ESP would reduce benzene emissions.

6.9 CARBON BLACK MANUFACTURE

The chemical carbon black consists of finely divided carbon produced by the thermal decomposition of hydrocarbons in the vapor phase, unlike coke that is produced by the pyrolysis of solids. Carbon black is a major industrial chemical used primarily as a reinforcing agent in rubber compounds, which accounts for over 90 percent of its use. It is used primarily in tires (both original equipment and replacement), which accounts for over 70 percent of its use. The control of the compounds include inner tubes and retreads. Other uses include automotive hoses and belts, wire and cable, roofing, pigment in inks and coatings and as a plastic stabilizer. As of January 1994, there were 24 carbon black manufacturing facilities in the United States. Over 75 percent of all carbon black production occurs in the States of Texas and Louisiana (36 and 40 percent, respectively). The location of all facilities and their estimated annual production capacities in 1993 are provided in Table 6-28. The manufacture of carbon black is of potential concern for benzene emissions because the predominantly used production process involves the combustion of natural gas and the high-temperature pyrolysis of aromatic liquid hydrocarbons.

TABLE 6-28. LOCATIONS AND ANNUAL CAPACITIES OF CARBON BLACK PRODUCERS IN 1994

Company	Facility Location	Annual Capacity, millions of pounds (millions of kg)
Cabot Corporation	Franklin, LA Pampa, TX Villa Platte, LA Waverly, WV	260 (118) 60 (27) 280 (127) 180 (82)
Chevron Corporation	Cedar Bayou, TX	20 (9)
Columbian Chemicals Company	El Dorado, AR Moundsville, WV North Bend, LA Ulysses, KS	120 (54) 170 (77) 220 (100) 85 (39)
Degussa Corporation	Arkansas Pass, TX Belpre, OH ^a New Iberia, LA	180 (82) 130 (59) 200 (91)
Ebonex Corporation	Melvindale, MI	8 (3.6)
General Carbon Company	Los Angeles, CA	1 (0.45)
Hoover Color Corporation	Hiwassee, VA	1 (0.45)
J.M. Huber Corporation	Baytown, TX Borger, TX Orange, TX	225 (102) 175 (79) 135 (61)
Sid Richardson Carbon and Gasoline Company	Addis, LA Big Springs, TX Borger, TX	145 (66) 115 (52) 275 (125)
Witco Corporation	Phoenix City, AL Ponca City, OK Sunray, TX	60 (27) 255 (116) 120 (54)
TOTAL		3,420 (1,551)

Source: Reference 177.

Note: This listing is subject to change as market conditions change, facility ownership changes, plants are closed down, etc. The reader should verify the existence of particular facilities by consulting current listings and/or the plants themselves. The level of benzene emissions from any given facility is a function of variables such as capacity, throughput, and control measures, and should be determined through direct contacts with plant personnel.

^a Emissions of 81,000 lb/yr (36,741 kg/yr) of benzene reported for 1992.¹¹¹

6.9.1 <u>Process Description for Carbon Black Manufacture</u>

Approximately 90 percent of all carbon black produced in the United States is manufactured by the oil-furnace process, a schematic of which is given in Figure 6-10. The process streams identified in Figure 6-10 are defined in Table 6-29. Table 6-29. Generally, all oil-furnace carbon black plants are similar in overall structure and operation. The most pronounced differences in plants are primarily associated with the details of decomposition furnace design and raw product processing.

In the oil-furnace process, carbon black is produced by the pyrolysis of an atomized liquid hydrocarbon feedstock in a refractory-lined steel furnace. Processing temperatures in the steel furnace range from 2,408 to 2,804°F (1,320 to 1,540°C). The heat needed to accomplish the desired hydrocarbon decomposition reaction is supplied by the combustion of natural gas.¹⁷⁸

Feed materials used in the oil-furnace process consist of petroleum oil, natural gas, and air. Also, small quantities of alkali metal salts may be added to the oil feed to control the degree of structure of the carbon black.¹⁷⁹ The ideal raw material for the production of modern, high structure carbon blacks is an oil which is highly aromatic; low in sulfur, asphaltenes and high molecular weight resins; and substantially free of suspended ash, carbon, and water. To provide maximum efficiency, the furnace and burner are designed to separate, insofar as possible, the heat generating reaction from the carbon forming reaction. Thus, the natural gas feed (Stream 2 in Figure 6-10) is burned to completion with preheated air (Stream 3) to produce a temperature of 2,408 to 2,804 °F (1,320 to 1,540 °C). The reactor is designed so that this zone of complete combustion attains a swirling motion, and the oil feed (Stream 1), preheated to 392 to 698 °F (200 to 370 °C), is sprayed into the center of the zone. Preheating is accomplished by heat exchange with the reactor effluent and/or by means of a gas-fired heater. The oil is cracked to carbon and hydrogen with side reactions producing carbon oxides, water, methane, acetylene and other hydrocarbon products. The heat

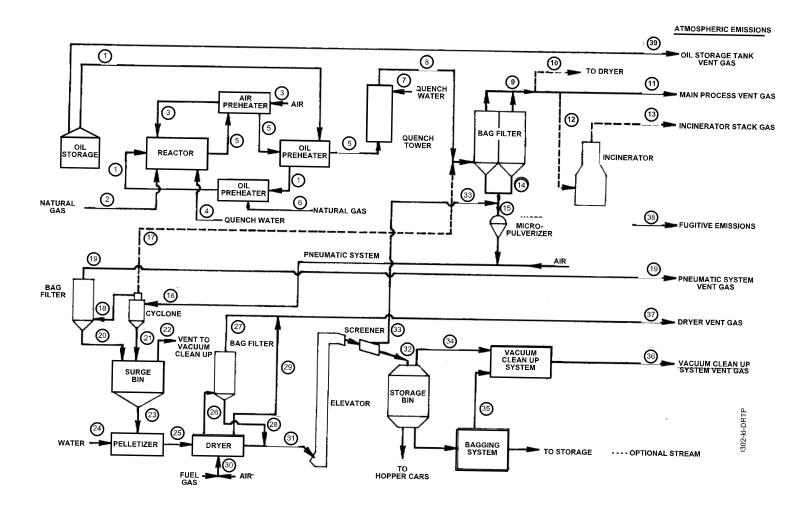


Figure 6-10. Process Diagram for an Oil-Furnace Carbon Black Plant

Source: Reference 179.

TABLE 6-29. STREAM CODES FOR THE OIL-FURNACE PROCESS ILLUSTRATED IN FIGURE 6-10

Stream	Identification	Stream	Identification
1	Oil feed	21	Carbon black from cyclone
2	Natural gas feed	22	Surge bin vent
3	Air to reactor	23	Carbon black to pelletizer
4	Quench water	24	Water to pelletizer
5	Reactor effluent	25	Pelletizer effluent
6	Gas to oil preheater	26	Dryer direct heat source vent
7	Water to quench tower	27	Dryer bag filter vent
8	Quench tower effluent	28	Carbon black from dryer bag filter
9	Bag filter effluent	29	Dryer indirect heat source vent
10	Vent gas purge for dryer fuel	30	Hot gases to dryer
11	Main process vent gas	31	Dried carbon black
12	Vent gas to incinerator	32	Screened carbon black
13	Incinerator stack gas	33	Carbon black recycle
14	Recovered carbon black	34	Storage bin vent gas
15	Carbon black to micropulverizer	35	Bagging system vent gas
16	Pneumatic conveyor system	36	Vacuum cleanup system vent gas
17	Cyclone vent gas recycle	37	Dryer vent gas
18	Cyclone vent gas	38	Fugitive emissions
19	Pneumatic system vent gas	39	Oil storage tank vent gas
20	Carbon black from bag filter		

Source: Reference 178.

transfer from the hot combustion gases to the atomized oil is enhanced by highly turbulent flow in the reactor. 179

The reactor converts 35 to 65 percent of the feedstock carbon content to carbon black, depending on the feed composition and the grade of black being produced. The yields are lower for the smaller particle size grades of black. Variables that can be adjusted to produce a given grade of black include operating temperature, fuel concentration, space velocity in the reaction zone, and reactor geometry (which influences the degree of turbulence in the reactor). A typical set of reactor operating conditions for high abrasion furnace carbon black is given in Table 6-30.¹⁷⁹

The hot combustion gases and suspended carbon black are cooled to about $1004\,^{\circ}F$ ($540\,^{\circ}C$) by a direct water spray in the quench area, which is located near the reactor outlet. The reactor effluent (Stream 5 in Figure 6-10) is further cooled by heat exchange in the air and oil preheaters. It is then sent to a quench tower where direct water sprays finally reduce the stream temperature to $446\,^{\circ}F$ ($230\,^{\circ}C$).

Carbon black is recovered from the reactor effluent stream by means of a bag filter unit. The raw carbon black collected in the bag filter unit must be further processed to become a marketable product. After passing through the pulverizer, the black has a bulk density of 1.50 to 3.68 lb/ft³ (24 to 59 kg/m³), and it is too fluffy and dusty to be transported. It is therefore converted into pellets or beads with a bulk density of 6.06 to 10.68 lb/ft³ (97 to 171 kg/m³). In this form, it is dust-free and sufficiently compacted for shipment.

6.9.2 Benzene Emissions from Carbon Black Manufacture

Although no emission factors are readily available for benzene from carbon black manufacture, one carbon black manufacturer with annual capacity of 130 million pounds (59 million kg) using the oil-furnace process reported benzene emissions of 81,000 lb/yr (36,741 kg/yr) for 1992, which translates to 6.23×10^{-4} lb (2.83×10^{-4} kg) benzene per lb (kg)

TABLE 6-30. TYPICAL OPERATING CONDITIONS FOR CARBON BLACK MANUFACTURE (HIGH ABRASION FURNACE)

Parameter	Value		
Rate of oil feed	$27 \text{ ft}^3/\text{hr} (0.76 \text{ m}^3/\text{hr})$		
Preheat temperature of oil	550°F (288°C)		
Rate of air feed	234,944 ft ³ /hr (6,653 m ³ /hr)		
Rate of natural gas feed	22,001 ft ³ /hr (623 m ³ /hr)		
Furnace temperature in reaction zone	2,552°F (1,400°C)		
Rate of carbon black production	860 lb/hr (390 kg/hr)		
Yield of black (based on carbon in oil feed)	60 percent		

Source: Reference 179.

carbon black produced. No regulations applicable to carbon black manufacture were identified that would affect benzene emissions. The emission factor is given in Table 6-31.¹¹¹

TABLE 6-31. EMISSION FACTOR FOR CARBON BLACK MANUFACTURE

SCC Number Description		Emission Factor (lb benzene/lb carbon black)	Emission Factor Rating	
Oil Furnace Process		6.23x10 ⁻⁴		

Source: Reference 111.

6.10 RAYON-BASED CARBON FIBER MANUFACTURE

Rayon-based carbon fibers are used primarily in cloth for aerospace applications, including phenolic impregnated heat shields and in carbon-carbon composites for missile parts and aircraft brakes. Due to their high carbon content, these fibers remain stable at very high temperatures.

A list of U.S. producers of rayon-based carbon fibers is given in Table 6-32. 177

TABLE 6-32. RAYON-BASED CARBON FIBER MANUFACTURERS

Manufacturer	Location		
Amoco Performance Products, Inc.	Greenville, SC		
BP Chemicals (Hitco) Inc.	Gardena, CA		
Fibers and Materials Division			
Polycarbon, Inc.	Valencia, CA		

Source: Reference 177.

6.10.1 <u>Process Description for the Rayon-Based Carbon Fiber Manufacturing Industry</u>

There are three steps in the production process of rayon-based carbon cloth:

- Preparation and heat treating;
- Carbonization; and
- High heat treatment (optional). 180

In the preparation and heat treating step, the rayon-based cloth is heated at 390 to 660°F (200 to 350°C). Water is driven off (50 to 60 percent weight loss) during this step to form a char with thermal stability. In the carbonization step, the cloth is heated to 1,800 to 3,600°F (1,000 to 2,000°C), where additional weight is lost and the beginnings of a carbon layer structure is formed. To produce a high strength rayon-based fiber, a third step is needed. The cloth is stretched and heat treated at temperatures near 5,400°F (3,000°C). 180

6.10.2 <u>Benzene Emissions from the Rayon-Based Carbon Fiber Manufacturing Industry</u>

Benzene emissions occur from the exhaust stack of the carbon fabric dryer, which is used in carbonization of the heat treated rayon. An emission factor for this source is given in Table 6-33. Bell

6.10.3 <u>Controls and Regulatory Analysis</u>

No controls or regulations were identified for the rayon-based carbon fiber manufacturing industry.

6.11 ALUMINUM CASTING

The aluminum casting industry produces aluminum products, such as aluminum parts for marine outboard motors, from cast molds. Sections 6.11.1 through 6.12.3 describe the aluminum casting process, benzene emissions resulting from this process, and air emission control devices utilized in the process to reduce benzene emissions.

The number of aluminum casting facilities in the United States was not identified.

6.11.1 <u>Process Description for Aluminum Casting Facilities</u>

A common method for making the mold for aluminum motor parts is to utilize polystyrene foam patterns or "positives" of the desired metal part. The basic principle of the casting operation involves the replacement of the polystyrene pattern held within a sand mold with molten metal to form the metal casting. Figure 6-11 presents a simplified flow diagram for a typical aluminum casting facility utilizing polystyrene patterns.

TABLE 6-33. EMISSION FACTOR FOR RAYON-BASED CARBON MANUFACTURE

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/lb (g/kg) ^a	Emission Factor Rating
3-64-920-000	Rayon-based Carbon Fibers	Carbon Fabric Dryer	Uncontrolled	7.17x10 ⁻⁷ (7.17x10 ⁻⁴)	В

Source: Reference 181.

^a Emission factor is lb (g) of benzene emitted per lb (kg) of rayon-based carbon produced.

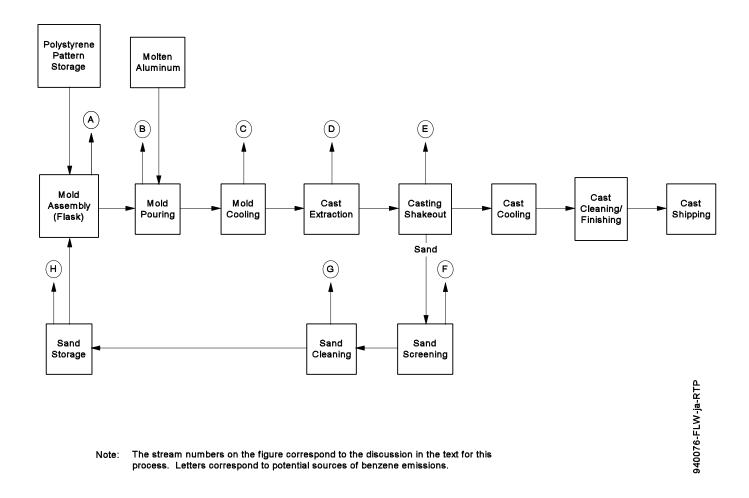


Figure 6-11. Flow Diagram of a Typical Aluminum Casting Facility

The aluminum casting process essentially consists of four stages: (1) mold assembly, (2) casting (i.e., mold pouring, mold cooling, and cast extraction), (3) cast cleaning and finishing (i.e., casting shakeout, cast cooling, and cast cleaning and finishing), and (4) sand handling (i.e., sand screening and cleaning). A polystyrene foam pattern is first coated with a thin layer of ceramic material for stability. The polystyrene foam pattern is placed within a metal flask. Sand is poured into the flask, surrounding and covering the pattern. The sand is compacted around the polystyrene pattern to form the mold. Low levels of benzene may be emitted from the sand fill operation, depending on the residue of organic matter remaining on the sand recycled from the casting shakeout process step. These emissions may be collected in a fume hood and vented to the atmosphere (Vent A in Figure 6-11).

The metal flask is moved to the pouring station where molten aluminum is poured into the mold. The foam vaporizes as it is displaced by the molten aluminum, which fills the cavity left within the sand mold. A majority of the foam vapors migrate into the sand and remain trapped in the sand until the casting shakeout process. Some of the vapors are released during the mold pouring event. These vapors are collected in a fume hood and vented to the atmosphere (Vent B in Figure 6-11).

The poured molds are conveyed within the flasks along a cooling conveyor, allowing the aluminum casting to harden. The cooling process may result in benzene emissions (as depicted as Vent C in Figure 6-11).

When the casting has formed and cooled sufficiently, the cast is extracted from the metal flask. Benzene may be emitted from this process step. The emissions are captured and vented to the atmosphere (Vent D in Figure 6-11).

The casting and flask are moved to the casting shake-out area, where sand used in forming the mold is dumped from the flask and removed from the casting by utilizing vibration to loosen the compacted sand. The collected sand (including pieces of molding) are

shaken, breaking up the sand mold. The majority of benzene emissions occur during this step. Vapors released by breaking the sand molds are captured and either treated with a catalytic incinerator or released to the atmosphere (Vent E in Figure 6-11).

The shaken sand is sent through a screen, then transported to a cleaning process for removal of remaining residue, such as a fluidized bed. Benzene emissions may be emitted during these process steps (depicted as Vents F and G in Figure 6-11). The cleaned sand is then transported to storage for reuse in the process.

Meanwhile, the casting, which has just undergone shakeout, is sent through a series of cooling, cleaning, and finishing steps to produce a final product. Benzene may be emitted from these process steps. The final products are stored to await shipping off-site.

6.11.2 <u>Benzene Emissions From Aluminum Metal Casting</u>

Benzene emissions from aluminum metal casting are produced by the vaporization of the polystyrene foam patterns used to form the molds, resulting from contact of the foam with molten aluminum. As described in Section 6.11.1, the polystyrene foam vapors migrate into the sand inside the mold, becoming trapped in the sand mold. As a result, most benzene emissions from the process are associated with sand handling activities, such as casting shake-out and sand screening. However, additional benzene is emitted from the casting steps, including mold pouring, mold cooling, and cast extraction.

Two test reports from two aluminum casting facilities were used to develop benzene emission factors. Both facilities utilized polystyrene foam patterns in their casting operations. One facility was equipped with a catalytic incinerator on its casting shakeout operation and a fabric filter on its sand cleaning operation (utilizing a fluidized bed for sand cleaning). The other facility was equipped with fabric filters on its mold assembly operation (i.e., filling the flask with sand), cast extraction, casting shakeout, and sand screening operations. Second cleaning operations.

General facility benzene emissions were measured at the two facilities. For one facility, general facility emissions consisted of emissions from the mold assembly, cast extraction, casting shakeout, sand screening, and sand storage operations, all of which were controlled by fabric filters. For the other facility, general facility emissions consisted of emissions from the mold assembly, mold pouring, cast extraction, casting shakeout, and sand cleaning operations, and only the cleaning operation was controlled with a fabric filter. Additionally, benzene emissions from the casting shakeout operation were measured both before and after the catalytic incinerator, yielding a benzene control efficiency of 89 percent. The emission factors associated with these emission data are shown in Table 6-34.

6.11.3 <u>Control Technologies for Aluminum Casting Operations</u>

Fabric filters are most commonly utilized for controlling emissions from aluminum casting operations; however, these control devices are not utilized for controlling benzene emissions, but are rather used to control fugitive dust emissions from sand handling. The only control device identified for controlling benzene emissions is a catalytic incinerator. As specified in Section 6.12.2, it has been demonstrated that catalytic incinerators achieve 89 percent reduction in benzene emissions.

No regulations were identified that control emissions of benzene from aluminum casting operations. However, a MACT standard for control of HAPs from secondary aluminum facilities is currently underway.

6.12 ASPHALT ROOFING MANUFACTURING

The asphaltic material that is obtained toward the end of the process of fractional distillation of crude oil is mainly used as asphalt paving concrete (discussed in Section 7.9) and for asphalt roofing. The asphalt roofing manufacturing process and the emissions associated with its manufacture are described in this section.

TABLE 6-34. EMISSION FACTORS FOR ALUMINUM CASTING

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/ton (kg/Mg) ^a	Emission Factor Rating
3-04-001-99	Secondary Metals- Secondary Aluminum- Not	General Facility (Vents A, D, E, F, and H)	Uncontrolled	$7.08x10^{-2} (3.54x10^{-2})$	D
	Classified	General Facility (Vents A, B, D, E, and G)	Uncontrolled	$7.47x10^{-2} (3.73x10^{-2})$	D
3-04-001-14	Secondary Metals-	Casting Shakeout Operation	Catalytic Incinerator	$6.09x10^{-3} (3.45x10^{-3})$	D
	Secondary Aluminum- Pouring/Casting		Uncontrolled	5.48x10 ⁻³ (2.74x10 ⁻²)	D

Source: Reference 181.

^a Emission factor is lb (kg) of benzene emitted per ton (Mg) of molten aluminum poured.

In 1992, there were 98 asphalt roofing manufacturing plants operating in the United States. A list of all current facilities, as identified by the Asphalt Roofing Manufacturers Association, is provided in Table 6-35.¹⁸⁴ Total national production in 1993 of asphalt roofing materials (saturated felts) was estimated at 557,487 tons (505,749 Mg).¹⁸⁴ States containing a relatively significant number of roofing plants include California (14),

Texas (14), Ohio (6), and Alabama (5). These four states contain approximately 40 percent of the total number of roofing facilities. The majority of all plants nationwide are located in urban as opposed to rural areas.

6.12.1 <u>Process Description</u>

The production of asphalt roofing materials is common owing to the widespread usage of these materials in the United States. The asphalt roofing industry manufactures asphalt-saturated felt rolls, shingles, roll roofing with mineral granules on the surface, and smooth roll roofing, which may contain a small amount of mineral dust or mica on the surface. Most of these products are used in roof construction, but small quantities are used in walls and other building applications. ¹⁸⁵

The asphaltic material derived from crude oil and used to make asphalt roofing products is also called asphalt flux. The handling and storing of asphalt flux is a potential source of benzene emissions. Asphalt is normally delivered to an asphalt roofing plant in bulk by pipeline, tanker truck, or railcar. Bulk asphalt delivered in liquid form may range in temperature from $200 \text{ to } 400\,^{\circ}\text{F}$ (93 to $204\,^{\circ}\text{C}$), depending on the type of asphalt and local practice. $^{186\text{-}188}$

With bulk liquid asphalt, the most common method of unloading is to couple a flexible pipe to the tanker and pump the asphalt directly into the appropriate storage tanks. The tanker cover is partially open during the transfer. Because this is a closed system, the

TABLE 6-35. ASPHALT ROOFING MANUFACTURERS

Company	Roofing Plant Location
Allied-Signal Incorporated	Detroit, MI Fairfield, AL Ironton, OH
Bird Incorported	Norwood, MA
The Celotex Corporation	Camden, AR Fremont, CA Birmingham, AL Goldsboro, NC Houston, TX Lockland, OH Perth Amboy, NJ San Antonio, TX Los Angeles, CA Memphis, TN
Certainteed Corporation	Shakopee, MN Oxford, NC Milan, OH
Elk Corportion of America	Ennis, TX Tuscaloosa, AL
Fields Corporation	Kent, WA Tacoma, WA
GAF Building Materials, Inc.	Baltimore, MD Dallas, TX Erie, PA Fontana, CA Millis, MA Minneapolis, MN Mobile, AL Mount Vernon, IN Savannah, GA Tampa, FL
Gate Roofing Manufacturing, Inc.	Green Cove Springs, FL
Georgia-Pacific Corporation	Ardmore, OK Daingerfield, TX Franklin, OH Hampton, GA Quakertown, PA

(continued)

TABLE 6-35. CONTINUED

Company	Roofing Plant Location
Globe Building Materials	Whiting, IN St. Paul, MN Chester, WV
GS Roofing Products Company, Inc.	Charleston, SC Ennis, TX Little Rock, AR Martinez, CA Peachtree City, GA Portland, OR Shreveport, LA Wilmington, CA
Herbert Malarkey Roofing Company	Portland, OR
IKO Chicago Incorporated	Chicago, IL
IKO Production Incorporated	Franklin, OH Wilmington, DE
Koppers Industries, Incorporated	Birmingham, AL Chicago, IL Follensbee, WV Houston, TX
Leatherback Industries	Alburquerque, NM Hollister, CA
Lunday-Thagard Company	South Gate, CA
Manville Sales Corporation	Fort Worth, TX Pittsburg, CA Savannah, GA Waukegan, IL
Neste Oil Services	Belton, TX Calexico, CA Fresno, CA Houston, TX Long Beach, CA Pittsburg, CA Salt Lake City, UT San Diego, CA

(continued)

TABLE 6-35. CONTINUED

Company	Roofing Plant Location
Owens-Corning Fiberglas Corporation	Atlanta, GA Brookville, IN Compton, CA Denver, CO Detroit, MI Houston, TX Irving, TX Jacksonville, FL Jessup, MD Kearny, NJ Medina, OH Memphis, TN Minneapolis, MN Morehead City, NC Oklahoma City, OK Portland, OR
PABCO Roofing Products	Richmond, CA Tacoma, WA
TAMKO Asphalt Products, Incorporated	Dallas, TX Frederick, MD Joplin, MO Phillipsburg, KS Tuscaloosa, AL
TARCO, Incorporated	North Little Rock, AR Belton, TX
U.S. Intec, Incorporated	Corvallis, OR Monroe, GA

Source: Reference 184.

only potential sources of emissions are the tanker and the storage tanks. The magnitude of the emissions from the tanker is at least partially dependent on how far the cover is opened.

Another unloading procedure, of which there are numerous variations, is to pump the hot asphalt into a large open funnel that is connected to a surge tank. From the surge tanks, the asphalt is pumped directly into storage tanks. Emission sources under the surge tank configuration are the tanker, the interface between the tanker and the surge tank, the surge tank, and the storage tanks. The quantity of emissions depends on the asphalt's temperature and characteristics.

After delivery, asphalt flux is usually stored at 124 to 174°F (51 to 79°C), although storage temperatures of up to 450°F (232°C) have been noted. The lower temperatures are usually maintained with steam coils in the tanks. Oil- or gas-fired preheaters are used to maintain the asphalt flux at temperatures above 200°F (93°C). 186-188

Asphalt is transferred within a roofing plant by closed pipeline. Barring leaks, the only potential emissions sources are at the end-points of the pipes. These end-points are the storage tanks, the asphalt heaters (if not the closed tube type), and the air-blowing stills.

Asphalt flux is used to make two roofing grades of asphalt: saturant and coating. Saturant and coating asphalts are primarily distinguished by the differences in their softening points. The softening point of saturant asphalts is between 104 to 165°F (40 and 74°C); coating asphalts soften at about 230°F (110°C). These softening points are achieved by "blowing" hot asphalt flux, that is, by blowing air through tanks of hot asphalt flux.

The configuration of a typical air-blowing operation is shown in Figure 6-12.¹⁸⁵ This operation consists primarily of a blowing still, which is a tank with a sparger fitted near its base. The purpose of the sparger is to increase contact between the blowing air and the asphalt. Air is forced through holes in the sparger into a tank of hot (400 to 470°F [204 to 243°C]) asphalt flux. The air rises through the asphalt and initiates an exothermic oxidation

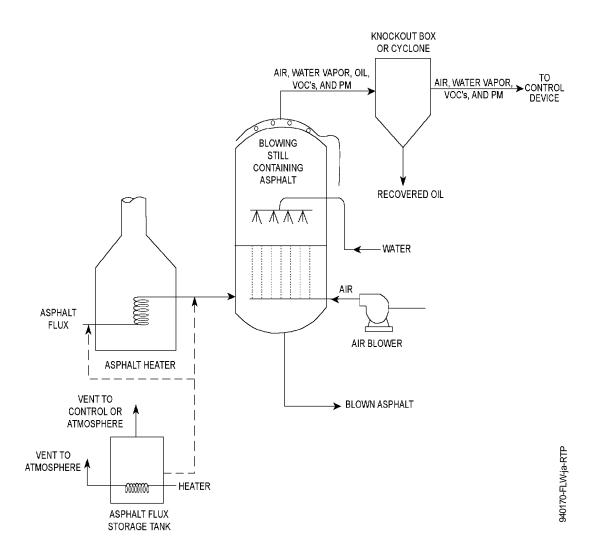


Figure 6-12. Asphalt Blowing Process Flow Diagram

Source: Reference 185.

reaction. Oxidizing the asphalt has the effect of raising its softening temperature, reducing penetration, and modifying other characteristics. Inorganic salts such as ferric chloride (FeCl₃) may be used as catalysts added to the asphalt flux during air blowing to better facilitate these transformations.¹⁸⁵

The time required for air blowing of asphalt depends on a number of factors including the characteristics of the asphalt flux, the characteristics desired for the finished product, the reaction temperature, the type of still used, the air injection rate, and the efficiency with which the air entering the still is dispersed throughout the asphalt. Blowing times may vary in duration from 30 minutes to 12 hours, with typical times from 1 to 4.5 hours. 185,186

Asphalt blowing is a highly temperature-dependent process because the rate of oxidation increases rapidly with increases in temperature. Asphalt is preheated to 400 to 470°F (204 to 243°C) before blowing is initiated to ensure that the oxidation process will start an acceptable rate. Conversion does take place at lower temperatures but is much slower. Because of the exothermic nature of the reaction, the asphalt temperature rises as blowing proceeds. This, in turn, further increases the reaction rate. Asphalt temperature is normally kept at about 500°F (260°C) during blowing by spraying water onto the surface of the asphalt, although external cooling may also be used to remove the heat of reaction. The allowable upper limit to the reaction temperature is dictated by safety considerations, with the maximum temperature of the asphalt usually kept at least 50°F (28°C) below the flash point of the asphalt being blown. ¹⁸⁶

The design and location of the sparger in the blowing still governs how much of the asphalt surface area is physically contacted by the injected air, and the vertical height of the still determines the time span of this contact. Vertical stills, because of their greater head (asphalt height), require less air flow for the same amount of asphalt-air contact. Both vertical and horizontal stills are used for asphalt blowing, but in new construction, the vertical type is preferred by the industry because of the increased asphalt-air contact and consequent reduction

in blowing times.¹⁸⁶ Also, asphalt losses from vertical stills are reported to be less than those from horizontal stills. All recent blowing still installations have been of the vertical type.

Asphalt blowing can be either a batch process or a continuous operation; however, the majority of facilities use a batch process. Asphalt flux is sometimes blown by the oil refiner or asphalt processor to meet the roofing manufacturer's specifications. Many roofing manufacturers, however, purchase the flux and carry out their own blowing.

Blown asphalt (saturant and coating asphalt) is used to produce asphalt felt and coated asphalt roofing and siding products in the processes depicted in Figures 6-13 and 6-14. The processes are identical up to the point where the material is to be coated. A roll of felt is installed on the felt reel and unwound onto a dry floating looper. The dry floating looper provides a reservoir of felt material to match the intermittent operation of the felt roller to the continuous operation of the line. Felt is unwound from the roll at a faster rate than is required by the line, with the excess being stored in the dry looper. The flow of felt to the line and the tension on the material is kept constant by raising the top set of rollers and increasing looper capacity. The opposite action occurs when a new roll is being put on the felt reel and spliced in, and the felt supply ceases temporarily. There are no benzene emissions generated in this processing step. ¹⁸⁶

Following the dry looper, the felt enters the saturator, where moisture is driven out and the felt fibers and intervening spaces are filled with saturant asphalt. (If a fiberglass mat web is used instead of felt, the saturation step and the subsequent drying-in process are bypassed.) The saturator also contains a looper arrangement, which is almost totally submerged in a tank of asphalt maintained at a temperature of 450 to 500°F (232 to 260°C). The absorbed asphalt increases the sheet or web weight by about 150 percent. At some plants, the felt is sprayed on one side with asphalt to drive out the moisture prior to dipping. This approach reportedly results in higher benzene emissions than does use of the dip process alone. The saturator is a significant benzene emissions source within the asphalt roofing process.

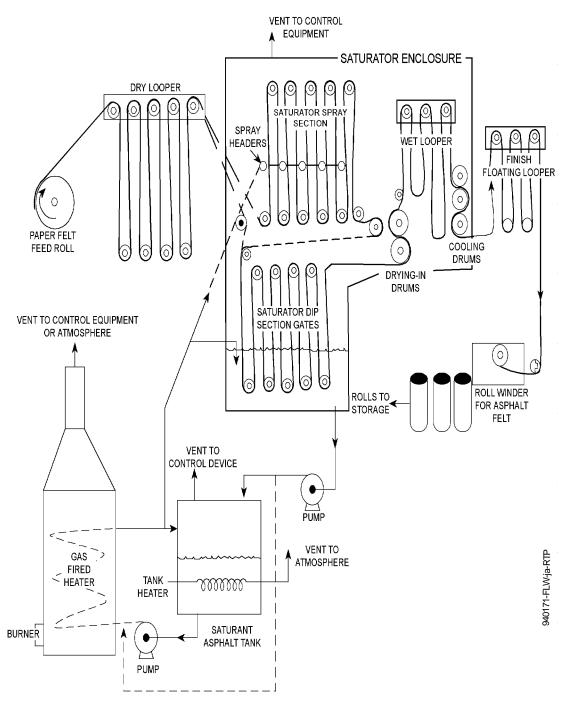


Figure 6-13. Asphalt-Saturated Felt Manufacturing Process

Source: Reference 185.

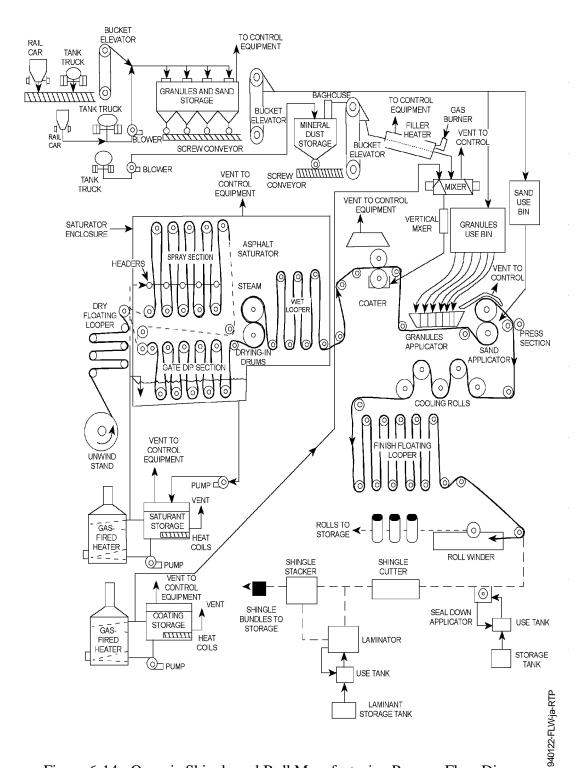


Figure 6-14. Organic Shingle and Roll Manufacturing Process Flow Diagram

Source: Reference 185.

The saturated felt then passes through drying-in drums and onto the wet looper, sometimes called the hot looper. The drying-in drums press surface saturant into the felt. Depending on the required final product, additional saturant may also be added at this point. The amount of absorption depends on the viscosity of the asphalt and the length of time the asphalt remains fluid. The wet looper increases absorption by providing time for the saturant asphalt to penetrate the felt. The wet looper operation has been shown to be a significant source of organic particulate emissions within the asphalt roofing process; however, the portion that is benzene has not been defined. 186,187

If saturated felt is being produced, the sheet passes directly to the cool-down section. For surfaced roofing products, however, the saturated felt is carried to the coater station, where a stabilized asphalt coating is applied to both the top and bottom surfaces. Stabilized coating contains a mineral stabilizer and a harder, more viscous coating asphalt that has a higher softening point than saturant asphalt. The coating asphalt and mineral stabilizer are mixed in approximately equal proportions. The mineral stabilizer may consist of finely divided lime, silica, slate dust, dolomite, or other mineral materials.

The weight of the finished product is controlled by the amount of coating used. The coater rollers can be moved closer together to reduce the amount of coating applied to the felt, or separated to increase it. Many modern plants are equipped with automatic scales that weigh the sheets in the process of manufacture and warn the coater operator when the product is running under or over specifications. The coater is a significant emissions source within the roofing production process. It releases asphalt fumes containing organics, some of which may be benzene compounds. 186,187

The function of the coater-mixer is to mix coating asphalt and a mineral stabilizer in approximately equal proportions. The stabilized asphalt is then piped to the coating pan. The asphalt is piped in at about 450 to 500 °F (232 to 260 °C), and the mineral stabilizer is delivered by screw conveyor. There is often a preheater immediately ahead of the

coater-mixer to dry and preheat the material before it is fed into the coater-mixer. This eliminates moisture problems and also helps to maintain the temperature above 320°F (160°C) in the coater-mixer. The coater-mixer is usually covered or enclosed, with an exhaust pipe for the air displaced by (or carried with) the incoming materials. The coater-mixer is viewed as a potential source of benzene emissions, but not a significant one. 186,187

The next step in the production of coated roofing products is the application of mineral surfacing. The surfacing section of the roofing line usually consists of a multi-compartmented granule hopper, two parting agent hoppers, and two large press rollers. The hoppers are fed through flexible hoses from one or more machine bins above the line. These machine bins provide temporary storage and are sometimes called surge bins. The granule hopper drops colored granules from its various compartments onto the top surface of the moving sheet of coated felt in the sequence necessary to produce the desired color pattern on the roofing. This step is not required for smooth-surfaced products. ¹⁸⁶

Parting agents such as talc and sand (or some combination thereof) are applied to the top and back surfaces of the coated sheet from parting agent hoppers. These hoppers are usually of an open-top, slot-type design, slightly longer than the coated sheet is wide, with a screw arrangement for distributing the parting agent uniformly throughout its length. The first hopper is positioned between the granule hopper and the first large press roller, and 8 to 12 inches (0.2 to 0.3 m) above the sheet. It drops a generous amount of parting agent onto the top surface of the coated sheet and slightly over each edge. Collectors are often placed at the edges of the sheet to pick up this overspray, which is then recycled to the parting agent machine bin by open screw conveyor and bucket elevator. The second parting agent hopper is located between the rollers and dusts the back side of the coated sheet. Because of the steep angle of the sheet at this point, the average fall distance from the hopper to the sheet is usually somewhat greater than on the top side, and more of the material falls off the sheet.

In a second technique used to apply backing agent to the back side of a coated sheet, a hinged trough holds the backing material against the coated sheet and only material

that will adhere to the sheet is picked up. When the roofing line is not operating, the trough is tipped back so that no parting agent will escape past its lower lip.

Immediately after application of the surfacing material, the sheet passes through the cool-down section. Here the sheet is cooled rapidly by passing it around water-cooled rollers in an abbreviated looper arrangement. Usually, water is also sprayed on the surfaces of the sheet to speed the cooling process. The cool-down section is not a source of benzene emissions.

Following cooling, self-sealing coated sheets usually have an asphalt seal-down strip applied. The strip is applied by a roller, which is partially submerged in a pan of hot sealant asphalt. The pan is typically covered to minimize fugitive emissions. No seal-down strip is applied to standard shingle or roll-goods products. Some products are also texturized at this point by passing the sheet over an embossing roll that imparts a pattern to the surface of the coated sheet. 186

The cooling process for both asphalt felt and coated sheets is completed in the next processing station, known as the finish looper. In the finish looper, sheets are allowed to cool and dry gradually. Secondly, the finish looper provides line storage to match the continuous operation of the line to the intermittent operation of the roll winder. It also allows time for quick repairs or adjustments to the shingle cutter and stacker during continuous line operation or, conversely, allows cutting and packaging to continue when the line is down for repair. Usually, this part of the process is enclosed to keep the final cooling process from progressing too rapidly. Sometimes, in cold weather, heated air is also used to retard cooling. The finish looper is not viewed as a source of benzene emissions.¹⁸⁶

Following finishing, asphalt felt to be used in roll goods is wound on a mandrel, cut to the proper length, and packaged. When shingles are being made, the material from the finish looper is fed into the shingle-cutting machine. After the shingles have been cut, they are

moved by roller conveyor to manual or automatic packaging equipment. They are then stacked on pallets and transferred by forklift to storage areas or waiting trucks. ¹⁸⁶

6.12.2 <u>Benzene Emissions from Asphalt Roofing Manufacture</u>

The primary benzene emission sources associated with asphalt roofing are the asphalt air-blowing stills (and associated oil knockout boxes) and the felt saturators. An emission factor for benzene emissions from the blowing stills or saturators is given in Table 6-36. Additional potential benzene emission sources may include the wet looper, the coater-mixer, the felt coater, the seal-down stripper, and air-blown asphalt storage tanks. Minor fugitive emissions are also possible from asphalt flux and blown asphalt handling and transfer operations. 186-188,190

Process selection and control of process parameters have been promoted to minimize uncontrolled emissions, including benzene, from asphalt air-blowing stills, asphalt saturators, wet loopers, and coaters. Process controls include the use of:¹⁸⁴

- Dip saturators, rather than spray or spray-dip saturators;
- Vertical stills, rather than horizontal stills;
- Asphalts that inherently produce low emissions;
- Higher-flash-point asphalts;
- Reduced temperatures in the asphalt saturant pan;
- Reduced asphalt storage temperatures; and
- Lower asphalt-blowing temperatures.

Dip saturators have been installed for most new asphalt roofing line installations in recent years, and this trend is expected to continue. Recent asphalt blowing still installations have been almost exclusively of the vertical type because of its higher efficiency and lower emissions. Vertical stills occupy less space and require no heating during oxidizing

TABLE 6-36. EMISSION FACTOR FOR ASPHALT ROOFING MANUFACTURE

SCC Number	Description	Emissions Source	Control Device	Emission Factor lb/ton (kg/Mg) ^a	Emission Factor Rating
3-05-001-01	Petroleum Industry - Asphalt Roofing - Asphalt Blowing - Saturant	Blowing Stills or Saturators	Uncontrolled	52 (26)	Е

Source: Reference 189.

^a Emission factor is in lb (kg) of benzene emitted per ton (Mg) of asphalt roofing produced.

(if the temperature of the incoming flux is above 400°F [204°C]). Vertical stills are expected to be used in new installations equipped with stills and in most retrofit situations. ¹⁸⁶

Asphalt fluxes with lower flash points and softening points tend to have higher emissions of organics because these fluxes generally have been less severely cracked and contain more low-boiling fractions. Many of these light ends can be emitted during blowing. Limiting the minimum softening and flash points of asphalt flux should reduce the amount of benzene-containing fumes generated during blowing because less blowing is required to produce a saturant or coating asphalt. Saturant and coating asphalts with high softening points should reduce benzene emissions from felt saturation and coating operations. However, producing the higher softening point asphalt flux requires more blowing, which increases uncontrolled emissions from the blowing operation.¹⁸⁶

Although these process-oriented emissions control measures are useful, emissions capture equipment and add-on emissions control equipment are also necessary in asphalt roofing material production facilities. The capture of potential benzene emissions from asphalt blowing stills, asphalt storage tanks, asphalt tank truck unloading, and the coater-mixer can and is being achieved in the industry by the use of enclosure systems around the emissions-producing operations. The enclosures are maintained under negative pressure, and the contained emissions are ducted to control devices. Potential emissions from the saturator, wet looper, and coater are generally collected by a single enclosure by a canopy type hood or an enclosure/hood combination.

No regulations were identified to control benzene emissions from hot-mix asphalt plants.

6.13 CONSUMER PRODUCTS/BUILDING SUPPLIES

This section covers benzene emissions from the application and use of consumer products rather than from the manufacture of such products. Because the types of consumer

products to which benzene emissions are attributed are so extensive, no list of manufacturers is presented here.

Benzene emissions from the use of consumer products and building supplies have been reported in the literature. One indoor air quality data base for organic compounds, shows that indoor benzene levels have been measured in residences, commercial buildings, hospitals, schools, and office buildings. Substantiated sources of these benzene emissions were attributed to tobacco smoke, adhesives (including epoxy resins and latex caulks), spot cleaners, paint removers, particle board, foam insulation, inks, photo film, auto exhaust, and wood stain. Although benzene emissions were detected from these consumer sources, no specific benzene emission factors were identified. In addition to these consumer sources, detergents have been identified as another possible source of benzene emissions.

In another report, aromatic hydrocarbons (most likely including benzene) were listed as a constituent in certain automotive detailing and cleaning products, including body-cleaning compounds and engine cleaners/degreasers/parts cleaners. However, no specific emission levels were given.¹⁹²

Naphtha (CAS number 8030-30-6) is a mixture of a small percentage of benzene, toluene, xylene, and higher homologs derived from coal tar by fractional distillation. Among its applications, naphtha is used as thinner in paints and varnishes and as a solvent in rubber cement. Because naphtha contains a small percentage of benzene, some benzene emissions would be expected from these products. However, no qualifiable benzene emissions from naphtha-containing products were identified.

The main control for reducing benzene emissions from consumer products is reformulation, such as substituting water or lower-VOC-emitting alternatives. 192

The federal government and several states are currently working on regulations for the benzene (or VOC) content of consumer products. Consumer products is a very diverse category and the products are used in a variety of applications. ¹⁹³